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INFLUENCE OF COPPER IONS ON ADHERENCE OF VITREOUS COATINGS TO STAINLESS STEEL

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SUMMARY

An investigation was made of the effect of copper oxide in promoting the adherence of vitreous coatings to AISI type 321 stainless steel. It was found that copper ions in the coating produced a significant increase in adherence on both pickled and sandblasted surfaces but that the effect of the copper decreased with increased firing temperature and increased firing time for the pickled specimens. X-ray examination of specimens revealed that the copper ions are reduced to metallic copper near the interface during firing; however, examination of sections with the metallographic microscope showed no selective corrosion of the stainless-steel surface.

It was observed that the curve obtained when plotting copper oxide content of the coating against adherence index was of the same type as that obtained for cobalt oxide on ingot iron. The similarity of these curves, when combined with other observations, was believed to imply that, in the case of 18-8 stainless steel, surface roughness is relatively unimportant to the development of bond between vitreous coatings and the metal.

INTRODUCTION

A research program aimed at obtaining a better insight into ceramic-to-metal bond mechanisms has been in effect in the Enameled Metals Laboratory at the National Bureau of Standards since 1951. The overall plan in this work has been to determine the effect of different variables on the adherence of vitreous coatings to metals and alloys and then to arrive at the most probable bonding mechanism, or mechanisms, to explain the observed behavior.

Eight reports have been published since the program was initiated (refs. 1 to 8). All eight have been concerned, either directly or indirectly, with the adherence of vitreous coatings to iron and low-carbon steel and five of the eight have been concerned directly with the action of "adherence oxides." The action of adherence oxides has received

special emphasis because it was felt, from the beginning, that, without an understanding of how certain metal oxides improve adherence, no theory for bond development between ceramic materials and metals could achieve general acceptance.

Three of the earlier investigations (refs. 1, 2, and 3) seemed to point to the galvanic corrosion theory of Dietzel (refs. 9 and 10) as explaining one important mechanism by which strong adherence develops on iron specimens when cobalt ions are present in the coating. According to this theory, the powerful bond is caused by a mechanical anchoring of the coating to an iron surface which has been roughened during firing by a local galvanic cell action. In one of the studies (ref. 2) a good correlation was found to exist between adherence index and the number of undercuts or anchor points in the iron surface and this finding suggested that a mechanical interlock between coating and metal may, in fact, play an important role in bond development. However, it was noted in later reports (refs. 3 and 5) that this mechanism cannot be considered as the whole explanation of adherence, even for cobalt-bearing ground coats on iron.

Recently, it was discovered that copper ions have a pronounced action in promoting adherence when present in a coating applied to stainless steel. Inasmuch as this was the first observation of a metal ion improving the adherence of a coating to any metal other than iron or low-carbon steel, it was decided to investigate the effect further. The goal in this particular phase study was to determine whether the action of the copper ions was similar to that of cobalt ions in coatings for iron or whether, on the contrary, the two actions were significantly different. As in the earlier investigations, the present work was carried out under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

MATERIALS AND PROCEDURE

A vitreous-type coating was selected for study. The mill batch of this coating (E-1) is given in table 1, while the composition of the base frit (109-0) is listed in table 2. No adherence oxides are present; therefore, no adherence develops when the coating is applied to ordinary steel.

The 109-0 base frit was used in preparing the E-1 coating only. In addition, five other coatings of the E-1 type were prepared in which the 109-0 frit was modified by additions of 0.5, 1.0, 2.0, 4.0, and 8.0 percent by weight of cupric oxide. The mill batch and milling procedure was the same for these coatings as for the E-1.

The alloy used in the investigation was AISI type 321 stainless steel. This is an austenitic 18-8 alloy stabilized against intergranular corrosion by the addition of titanium in an amount equal to five times the carbon content. A total of 274 specimens, 4 inches square, was sheared from a single lot of 18-gage sheet. Half of the resulting specimens were cleaned by pickling for 15 minutes at 190° F in a solution with the following proportions of ferric chloride, hydrochloric acid, and water:

Ferric chloride ($FeCl_3.6H_2O$), g	100
Hydrochloric acid (concentrated), ml	50
Water, ml	850

The other half of the specimens were sandblasted using an air pressure of 80 psi and a silica sand sized to pass a No. 20 U. S. Standard sieve and be retained on a No. 100.

The coatings were applied to the specimens by dipping, the coating slip in each case being adjusted to give a fired thickness in the range 0.004 to 0.005 inch. The specimens were fired in an electrically heated box furnace at temperatures varying from 1,450° to 1,750° F.

Immediately after firing, the adherence indices were evaluated for each set of seven specimens with the Porcelain Enamel Institute Adherence Meter used as specified by the A.S.T.M. procedure (ref. 11). Selected specimens from the adherence determination were later sectioned and examined with a metallographic microscope.

RESULTS AND DISCUSSION

Effect of Firing Temperature

Figure 1 shows the effect of firing for 5 minutes at four different temperatures on the adherence of two coatings (copper-free and copper-bearing) when applied to stainless-steel specimens cleaned both by sandblasting and by pickling.

It will be noted from this figure that there is a general tendency for the copper oxide to increase the adherence index for both sandblasted and pickled specimens. This tendency is especially noticeable at the normal firing temperature of the coating (1,550° F); it is less well defined when the coating is underfired (1,450° F) or overfired (1,750° F).

Effect of Firing Time

Figure 2 shows the effect of firing time at 1,550° F. Again, in these curves, the tendency is for copper to improve the adherence to both the sandblasted and pickled specimens. In the case of the pickled specimens the effect of the copper becomes less and less as the firing time is increased beyond 4 minutes, but for the sandblasted specimens the effect of the copper is still pronounced after 32 minutes of firing. In contrast, the adherence of the copper-free coating on sandblasted specimens is excellent after the 2- and 4-minute firings but falls rapidly to a low value after the 8-minute treatment.

Effect of Copper Oxide Content

Figure 3 shows the curve obtained when the copper oxide content of the coating was plotted against adherence index as compared with a similar curve for cobalt-bearing coatings on ingot iron. The data for the comparison curve were obtained in an earlier study (ref. 2) in which the same E-1 coating was modified by adding cobalt oxide rather than copper oxide to the basic frit. In both cases, the coatings were applied to pickled metal.

The similarity of the two curves is immediately apparent. Both peak at approximately 1 percent added oxide and both begin to fall off with increasing oxide content. Such a close similarity in behavior suggests that the mechanism responsible for the bond development may be the same in both cases.

Microscopic Examination

Representative specimens were sectioned and examined with the metallographic microscope. This examination showed that the presence of copper ions in the coating had no detectable influence on the roughness of the interface.

The difference in the appearance of the interface between a cobalt-bearing coating on ingot iron and a copper-bearing coating on stainless steel is well brought out by the photomicrographs of figure 4. In both systems, the presence of the metal ions increases adherence by a substantial amount, but only in the case of the cobalt-bearing coating on iron is this increase accompanied by an increase in surface roughness. Although the roughness of the stainless-steel interface was, from all appearances, unchanged, the adherence index increased from 2.0 for the coating with no copper oxide to 67.0 for a coating containing 1 percent.

It was believed possible that roughness might be generated on a finer scale for copper-bearing coatings on stainless steel than for cobalt-bearing coatings on iron. For this reason, an examination of the sections was made using an oil-immersion objective giving a magnification of about 2,000. Again no change in roughness with copper content was detected. When viewed at this high magnification, however, a layer of metallic-looking crystallites was observed near the interface. This layer was present in all of the coatings that contained copper and was on the order of 0.0003 inch thick. The crystallites, which were copper colored, appeared to be embedded in a glassy matrix. The region or band containing the crystallites was separated from the surface of the stainless steel by a thin dark layer, approximately 0.000015 inch thick. The crystallites became larger with increased copper content of the coating, but the thickness of both the region containing crystallites and the dark intermediate layer appeared to be independent of copper content over the range 0.2 to 8.0 percent by weight of copper oxide.

X-Ray Examination

Earlier work using Co^{60} as a tracer showed that cobalt metal plates out during firing of a cobalt-bearing ground coat on iron (ref. 1). Copper does not act as an adherence promoter in coatings on iron, but it does on stainless steel. The presence of the metallic crystallites near the interface gave some indication that copper ions were being reduced at or near the stainless-steel surface, but identification of the crystallites as metalic copper could not be made with certainty by microscopic methods alone.

Consideration was given to use of a radioactive isotope of copper as a tracer, but unfortunately copper has no radioactive isotopes of sufficiently long half-life for work of this type.[1]

Identification of the crystallites was therefore attempted by X-ray methods. In this work, tabs 1 inch square were cut from fired specimens and mounted in Lucite with the coated side up. X-ray fluorescent spectra and X-ray diffraction patterns were first obtained from the coating surface, after which the mounts were transferred to a lap and approximately 0.001 inch of coating material was ground away. Both types of X-ray data were again obtained; the entire procedure was then repeated until all of the coating material had been removed and the stainless-steel surface was exposed.

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[1] Cu^{64} has a half-life of 12.88 hours and is a strong gamma emitter. Such an isotope, if it were rushed from the pile and used immediately, might give information of value. The short half-life, however, would restrict its usefulness.

Because of the transparency of the vitreous coating to X-radiation, it was not possible to establish any systematic relationship between the fluorescent spectral line intensities of copper and the distance of the examined surface from the coating-metal interface. On the other hand, the X-ray diffraction measurements on specimens from which the coating was almost entirely ground away clearly showed the presence of metallic copper. This result established that copper ions in the coating are reduced at or near the interface during the firing operation.

IMPLICATIONS OF RESULTS TO ADHERENCE THEORIES

As mentioned in the Introduction, practically all of the earlier work in this laboratory has pointed quite strongly to a close correlation between adherence and the roughness of the iron surface (ref. 2). Likewise, in the present investigation it was observed that in all cases better adherence developed on a rough sandblasted stainless-steel specimen than on a smooth pickled surface. Such an observation, by itself, suggests that surface roughness also plays an important role in the development of bond between vitreous coatings and stainless steel.

A closer inspection of the data, however, brings out two observations that tend to rule out roughness as a factor in bond development. First, the adherence of the copper-free coating on sandblasted specimens was found to fall off rapidly with both firing time and firing temperature; yet, at the same time, there was little if any decrease in the roughness of the interface. Second, the presence of copper ions substantially improved bond without promoting any selective attack on the stainless-steel surface.

These two observations appear to rule out roughness as a controlling factor in the adherence of coatings to stainless steel. In fact, the similarity of the two curves shown in figure 3 indicates that roughness may also be relatively unimportant in the case of coatings on iron. These two curves are enough alike to suggest that the same basic bonding mechanism is active when a cobalt-bearing coating is applied to iron as when copper-bearing coatings are applied to stainless steel. In both cases the metal ions are reduced and plate out as metal at or near the interface. The plating-out reaction is accompanied by a formation of metal oxide at the specimen surface in accordance with the following reaction:

$$M'O + M \longrightarrow MO + M' \qquad (1)$$

where $M'O$ is the adherence oxide and M is the metal to which the coating is applied.

It seems conceivable that it is the metal oxide formed from the plating-out reaction and not the action of the plated-out metal that is largely responsible for the bond development. If this is the true picture, then the correlations observed earlier between the number of anchor points and adherence index for coatings on iron (ref. 2) could be considered as fortuitous.[2] In other words, the anchor points could be an index to the amount of oxide formed from reaction (1) listed above and it could be the presence of this oxide rather than the anchor points that was largely responsible for bond development. The oxide would not necessarily be present as a discrete layer as proposed by Kautz (refs. 12 and 13) but rather as an oxide-enriched layer of coating material. It is believed obvious that more research is needed to investigate fully the various possibilities.

National Bureau of Standards,
Washington, D. C., July 30, 1955.

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[2]This possibility was suggested in an earlier paper on the galvanic corrosion theory (ref. 3).

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TABLE 1.- MILL BATCH OF E-1 COATING

[Milling time, 3 hr; fineness, 10g on 200 mesh from 50 ml of slip]

Material	Weight, g
Frit	1,000
Enameler's clay	60
Borax	10
Water	425

TABLE 2.- BATCH AND COMPUTED OXIDE COMPOSITION OF 109-0 FRIT

(a) Batch composition

Material	Parts by weight
Potash feldspar	30.82
Borax (hydrated)	44.25
Flint	30.50
Soda ash	9.16
Soda niter	5.15
Fluorspar	8.30
	128.18

(b) Computed oxide composition

Oxide	Percent by weight
SiO_2	51.0
B_2O_3	16.1
Al_2O_3	5.7
Na_2O	15.4
K_2O	3.5
CaF_2	8.3
	100.0

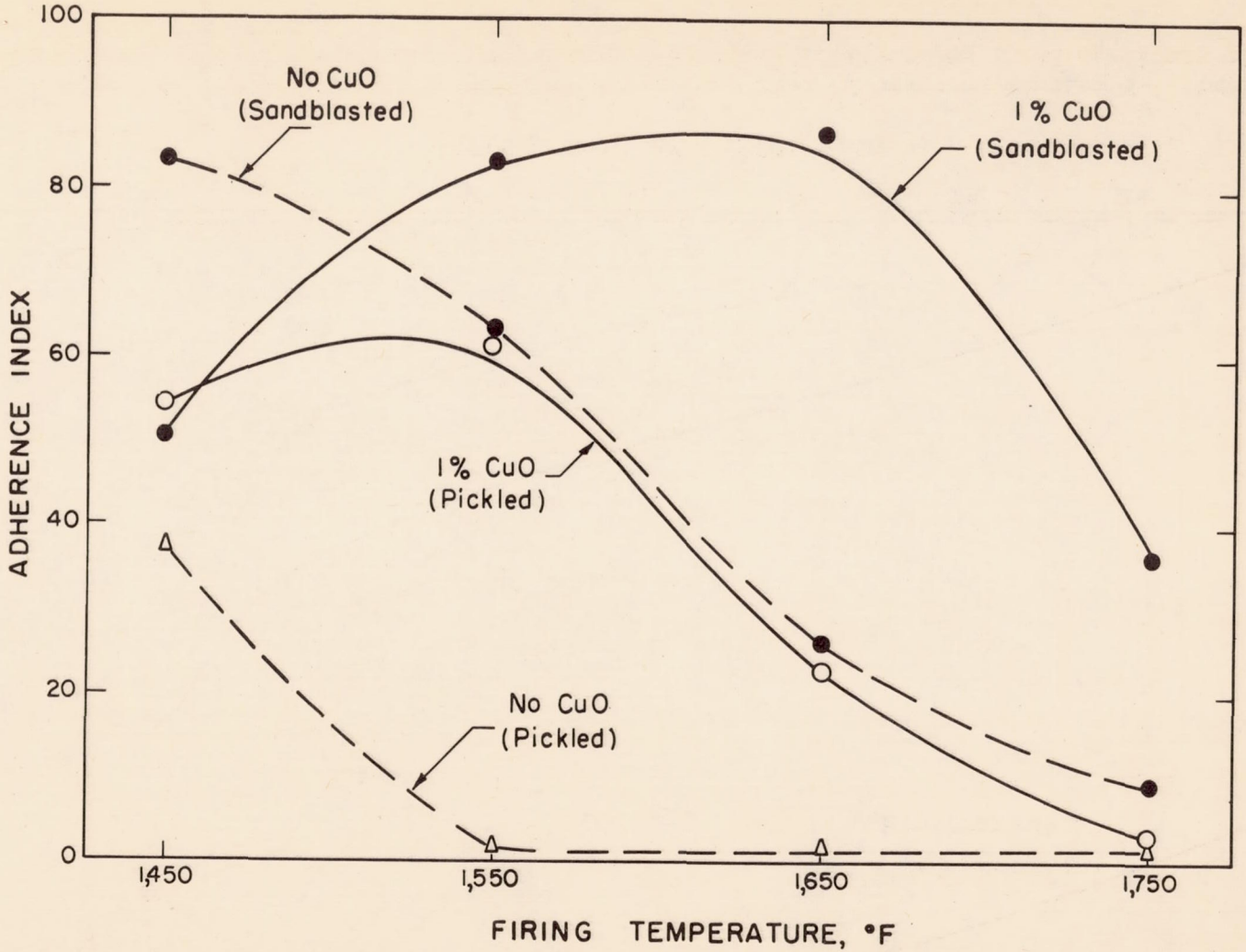


Figure 1.- Effect of firing temperature on adherence index of vitreous coating E-1, both with and without copper oxide, when fired for 5 minutes on 18-gage AISI type 321 stainless-steel specimens cleaned by two different treatments.

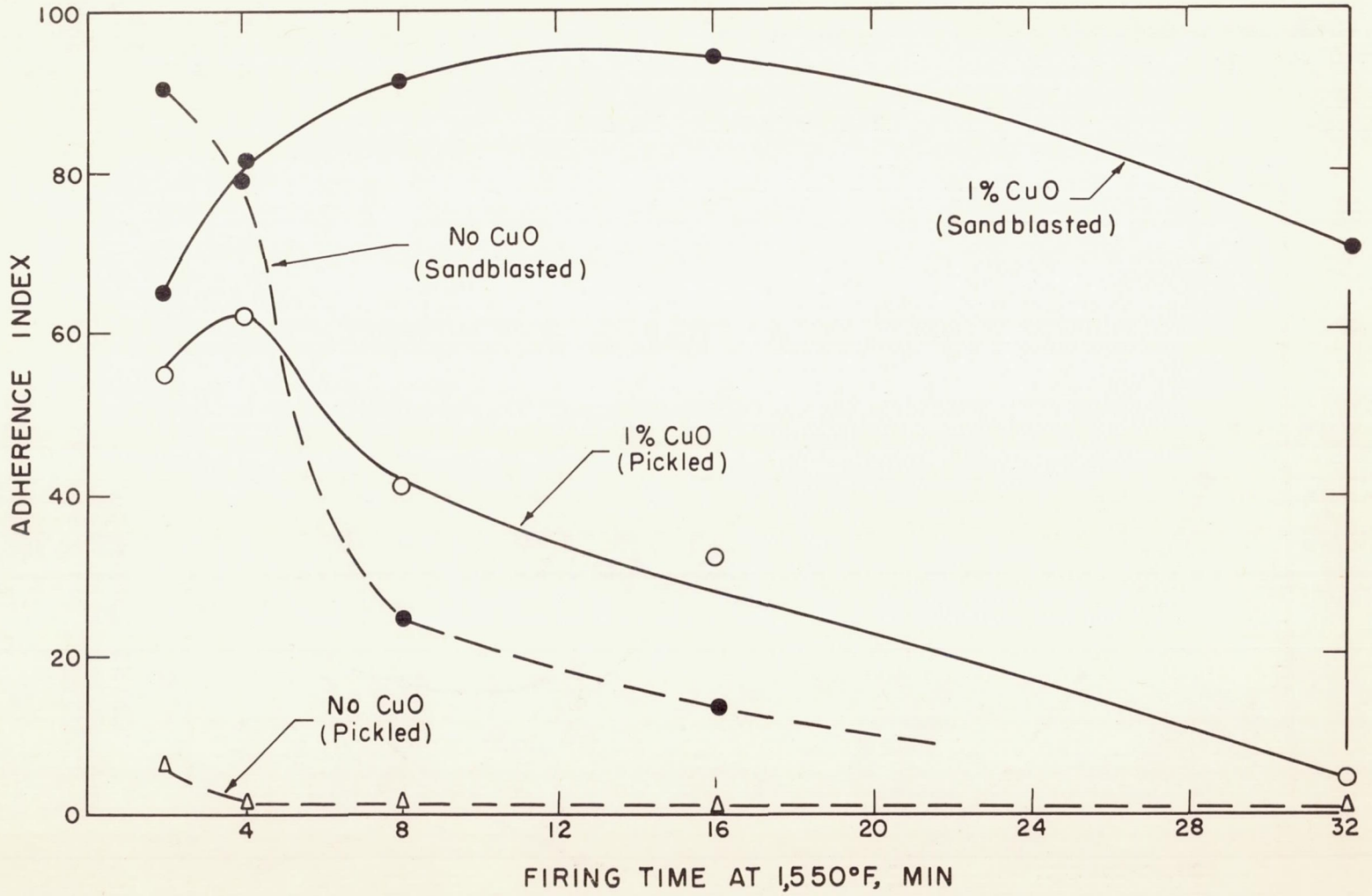


Figure 2.- Effect of firing time at 1,550° F on adherence index of vitreous coating E-1, both with and without copper oxide, when fired on 18-gage AISI type 321 stainless-steel specimens cleaned by two different treatments.

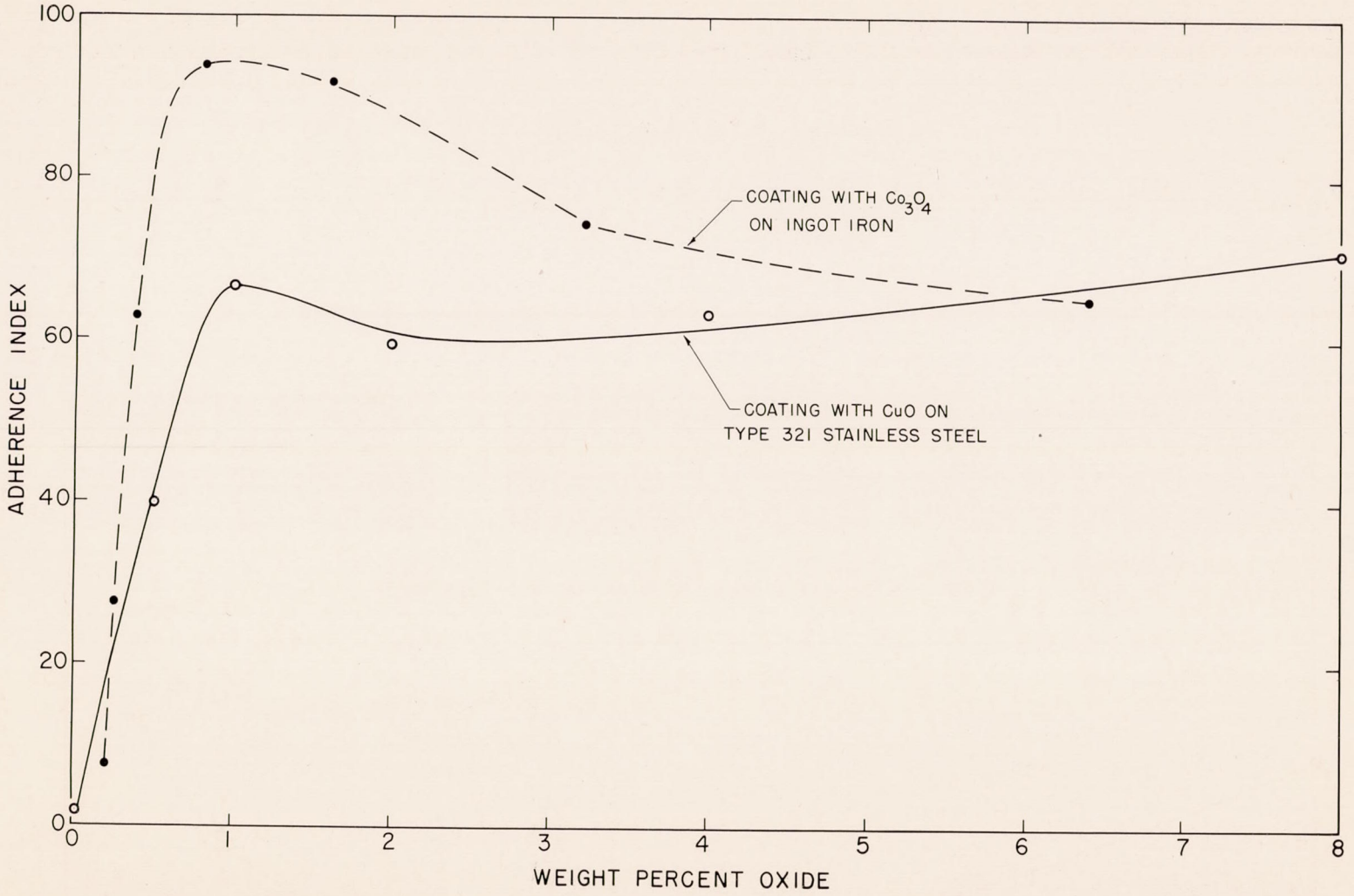
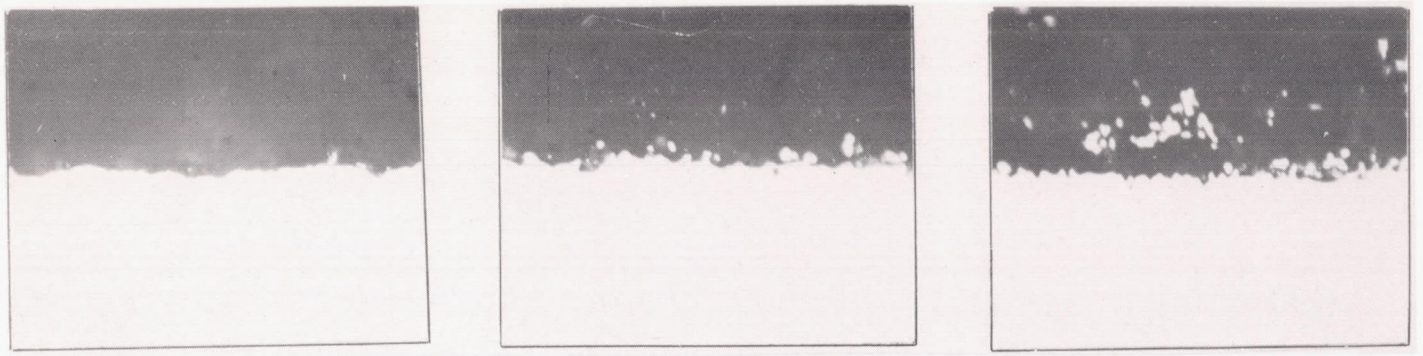


Figure 3.- Comparison of adherence-promoting effect of CuO in E-1 type of coating applied to 18-gage AISI type 321 stainless steel with effect of Co_3O_4 in same type of coating applied to 18-gage ingot iron. Specimens were cleaned by pickling; firing was for 5 minutes at 1,550° F.

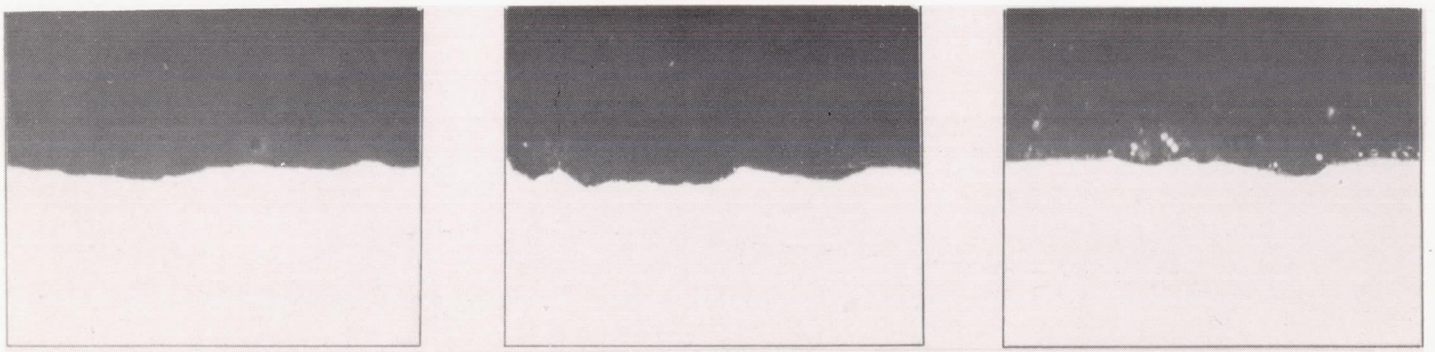


0.1 percent Co_3O_4;
adherence index, 4.9

0.8 percent Co_3O_4;
adherence index, 93.9

6.4 percent Co_3O_4;
adherence index, 65.3

(a) Cobalt-bearing coatings on ingot iron.



No copper oxide;
adherence index, 2.0

1.0 percent CuO;
adherence index, 67.0

8.0 percent CuO;
adherence index, 71.0

(b) Copper-bearing coatings on stainless steel.

Figure 4.- Interfaces between coatings of increasing copper oxide content on pickled AISI type 321 stainless steel and coatings of increased cobalt oxide content on ingot iron. Unetched; X750.

NACA - Langley Field, Va.